Ex-situ mineral carbonation with regenerative ammonium salts

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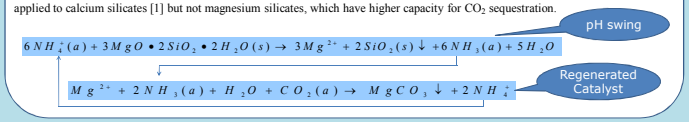
Introduction

✓ Ex-situ mineral carbonation is a process which permanently and safely stores CO_2 in solid Mg- and/or Ca- carbonates.

✓ Mineral carbonation bears high cost due to the pre-treatment needed to increase reaction rate. The pre-treatment methods include heat or chemical (acid) treatment.

✓ Another barrier of ex-situ is a large demand for expensive chemicals for changing pH.

✓ Ammonium salts could reduce the cost as a regenerative catalyst to accelerate the reaction rate and swing pH. This have been applied to calcium silicates [1] but not magnesium silicates, which have higher capacity for CO_2 sequestration.



Aim and objectives

Develop a new pH-swing process route for mineral carbonation with recyclable ammonium salts.

✓ Improve the dissolution rate of Mg-silicates with ammonium salts and investigate the carbonation of Mg-silicates with ammonia.

✓ Validate the pH swing cycle and prove the production of ammonia and the reproduction of ammonium salts during dissolution and carbonation.

Methodology

✓ Set up a high temperature and high pressure stirred reactor with Raman spectroscopy probe which can measure in-situ the concentration of molecules and ions in gas, solid and liquid phases (Fig.1).

✓ Compare the ammonium salts dissolution with traditional acid dissolution. The most efficient method to extract Mg/Ca cations from minerals is using sulfuric acid [2], but it brings high costs for chemicals and energy penalty in order to increase pH. Otherwise ammonium salts need heat pre-treatment to get high reaction rate, but it can swing pH without extra chemicals and can be reused.

✓ Investigate Mg/Ca-silicates carbonation with ammonia water at elevated conditions, measure the extent of carbonation conversion and identify the formation of magnesite precipitated.

Fig 1: High temperature and high pressure reactor system

Sample characterization

✓ Particle size: 75-150 μm used for this work (Grinding by Tema mill)

✓ Pre-treatment: heat activation up to 650 °C for an hour to produce heat-treated (HT) serpentine.

✓ The surface area (BET-N_2) increase after heat activation (Table 1)

Table 1: Surface area of serpentine, olivine and HT serpentine

Serpentine	8.09-10.13 m^2/g
HT-serpentine	10.15-15.71m^2/g
Olivine	2.74-4.22 m^2/g

✓ Mg weight content increase after heat activation (Table 2)

Table 2: SEM_EDX results of serpentine

Element	Parent Serpentine (wt%)	HT serpentine (wt%)
Mg	24.45	27.15
Ca	0.14	0.12
Fe	4.05	4.55
Si	17.92	19.57

Dissolution Studies

✓ There were 24 dissolution experiments carried out, the conditions are listed in Table 3.

Table 3: Conditions of dissolution studies

	Ammonium salts	Sulfuric acid
Samples	Serpentine, HT Serpentine	Serpentine
Chemicals	2 mol/L ammonium chloride (NH_4Cl), 1 mol/L ammonium sulfate ($(NH_4)_2SO_4$)	2 mol/L sulfuric acid (H_2SO_4)
Temperature (°C)	70, 120, 180, 220	30, 50, 70
Pressure (bar)	5-20	5-20
Solid/Liquid ratio (g/L)	25	25

✓ Ammonium salts extract Mg/Ca cations, and the extraction rate is around 15% (Fig. 2). By using HT-serpentine, the extraction rate increases significantly to 60% (Fig. 2).

✓ 44 % Mg extraction is achieved at 120 °C, compared to 12% reported by Lacker et al. (2007) [3] using ammonium satls but without heat pre-treatment.

✓ 52 % is achieved at 180 °C, compared to 70% in work by Gredemann and O'Connor's (2007) [4] using KOH and $NaHCO_3$ with heat pre-treatment, but the chemicals used were not regenerative.

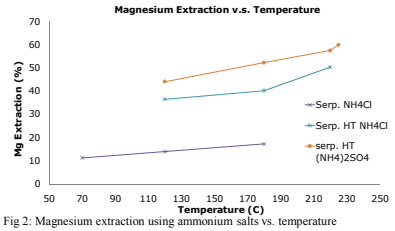


Fig 2: Magnesium extraction using ammonium salts vs. temperature

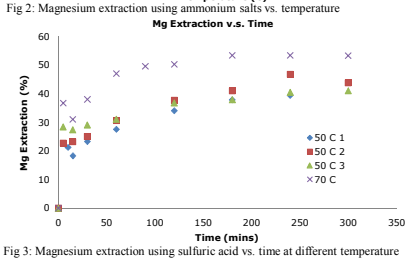


Fig 3: Magnesium extraction using sulfuric acid vs. time at different temperature

✓ The ammonium salts gave around 50% Mg^{2+} extraction rate at 120°C which was also seen with H_2SO_4 at 70°C (Fig 2 and 3).

✓ pH swing was observed from 5 to 7.5 for NH_4Cl, and 5.5 to 8.5 $(NH_4)_2SO_4$ (Table 4).

Table 4: pH change after dissolution experiment

	pH Start	pH Final
NH_4Cl	5.02	7.63
$(NH_4)_2SO_4$	5.55	8.50

✓ Ammonia was formed in reaction.

Conclusions

✓ HT serpentine shows much better performance than serpentine in terms of Mg extraction by ammonium salts.

✓ The Mg extraction efficiency of ammnium salts is similar to traditional acid. Moreover, ammonium salts can swing pH to favor carbonation and they can be regenerated after carboantion.

Future Plan

✓ Carbonation experiments are now being conducted (Table 5).

Table 5: Conditions of carbonation studies

	Ammonium salts
Samples	HT Serpentine
Chemicals	2 mol/L Ammonium chloride (NH_4Cl), 1 mol/L Ammonium sulfate ($(NH_4)_2SO_4$)
Temperature (°C)	120 °C, 180 °C, 220 °C
Pressure (bar)	10-150 bar
Solid/Liquid ratio (g/L)	25 g/L

✓ Measurement of ammonium salts concentration in solution (IC).

✓ Measurement of ammonia concentration in solution.

✓ Characterize the solids produced (TGA and Raman probe).

References

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